

Enhanced Reverse Saturable Absorption and Optical Limiting in Heavy-Atom Substituted Phthalocyanines

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ABSTRACT

The reverse saturable absorption and optical limiting response of metal phthalocyanines can be enhanced by using the heavy-atom effect. Phthalocyanines containing heavy metal atoms, such as In, Sn, and Pb show nearly a factor of two enhancement in the ratio of effective excited-state to ground-state absorption cross sections compared to those containing lighter atoms, such as Al and Si. In an f/8 optical geometry, homogeneous solutions of heavy metal phthalocyanines, at 30% linear transmission, limit 8-ns, 532-nm laser pulses to $\leq 3 \mu\text{J}$ (the energy for 50% probability of eye damage) for incident pulses up to 800 μJ .

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Materials that exhibit reverse saturable absorption are currently of interest for use in optical limiting devices for protection of sensors and eyes from energetic light pulses. Reverse saturable absorption (RSA) can occur when states with absorption cross sections (σ_e) in excess of the ground-state cross section (σ_g) are produced. RSA in the visible spectrum due to electronic excitation has been reported for several classes of organic chromophores.¹⁻⁷ The effectiveness of RSA molecules for optical limiting is determined **mainly** by the ratio of cross sections (σ_e/σ_g), which is function of wavelength, and the populations of the states that evolve in time during the pulse. There is considerable interest in approaches to enhancing the performance of RSA chromophores.

RSA and optical limiting in **metallophthalocyanines** (MPc) such as chloroaluminum phthalocyanine (CAP) and **bis(tri-(n-hexyl)siloxy) silicon naphthalocyanine** (SiNc) has been **investigated**^{4,7}, on picosecond and nanosecond timescales at 532-nm. Picosecond experiments showed that σ_s/σ_g , where s refers to the excited -singlet state, were 10.5 and 14, for CAP and SiNc, respectively. Nanosecond measurements on CAP⁸ and SiNc⁹ indicate that σ_t/σ_g values (t \equiv triplet state) are about 20 to 50. However, the triplet populations achievable during nanosecond pulses are limited by the small intersystem crossing rates, k_{isc} , for these **molecules**.^{9,10} These observations suggested to us the use of the “heavy-atom” effect as an approach to enhancing the optical limiting performance of **phthalocyanines**. By increasing the atomic number of the central metal atom, k_{isc} for the π -electronic states can be **increased**,¹⁰ allowing more efficient population of the triplet state.

In this paper, we examine the RSA performance of MPc's containing metals from groups 111A (Al, Ga, In) and IVA, (Si, Ge, Sn and Pb). For the Al, Ga and InPc's the molecular structures were of the form **(tri-(n-hexyl)siloxy) MPc**, whereas the Si, Ge, and SnPc's, of the form **bis(tri-(n-hexyl)siloxy)** and PbPc was of the form **Pbtetra(t-butyl)Pc**. These molecules were synthesized according to literature methods.¹¹ The electronic absorption spectrum of SnPc is shown in Figure 1, which reveals a strong “Q-band” absorption at 678 nm and a region of weak absorption from ~ 450 to 600 nm. Also shown is the transient triplet-triplet absorption spectrum, which

shows a maximum at 510 nm and a bandwidth of -130 nm. The ground-state and triplet-triplet spectra for the other molecules were quite similar, with a slight red shift of the Q-band as the metal becomes heavier.

The triplet quantum yields (Φ_t) and the first excited -singlet lifetimes (τ_s) are given, in Table 1, for the group 111A and IVA MPC's. Indeed, the τ_s values decrease and the Φ_t values increase as the metal becomes heavier, Thus, the triplet population achievable during a Q-switched laser pulse (e.g 8 ns) is significantly enhanced for the molecules with large Φ_t values. To the extent that the σ_g , σ_s and σ_t values are each similar for the different molecules, one would expect trends of increased nonlinear absorption for the heavier metal Pc's, for pulse widths between -0.5 and 25 ns.

Nanosecond nonlinear transmission measurements were performed using a frequency-doubled Q-switched Nd:YAG laser operating in a near Gaussian transverse mode with an 8-ns (FWHM) multimode pulse envelope. The laser pulses were focussed at the center of 1-cm pathlength solution cells by a 15-cm focal length, 2.5 cm diameter "best form" lens (f/40 geometry) giving a waist spot size of -13 μm (HW1/e²M) and a cell entrance spot size of -63 μm . The transmitted energy was collected by a 2.5 cm diameter, 15 cm focal length lens located to relay the collected energy to a nominal spot size of -2.0 mm on a photodiode of 1 cm diameter. This geometry afforded essentially total integrated energy detection, as was verified by the following experiment. Measurements with a 50% transmitting aperture stop in front of the detector performed on SiNc in a series of solvents with varying thermal refractive index coefficients (i.e., nitrobenzene to carbon disulfide) showed different transmission responses, whereas without the aperture the responses were the same, thus demonstrating the insensitivity of the unapertured detection to refractive spot size changes for pulse energies up to the highest values used.

Nonlinear transmission data obtained with 532-nm, 8-ns laser pulses, for the two series of MPC's are shown in Figure 2. At incident fluences below about 2 mJ/cm², the transmittance coincides with that measured using a spectrophotometer. The nanosecond pulse data for the two series of molecules show the trend of increased nonlinear absorption as the metal becomes

heavier, consistent with an enhanced triplet contribution. Measurements on the group IVA MPc's were also performed using 70-picosecond pulses, which are short compared to the timescales for triplet formation in these molecules. The Si, Ge and SnPc's showed the opposite trend of the nonlinear transmittance compared to that for the nanosecond pulses. Since the σ_g values are all about $\sim 2.3 \times 10^{-18} \text{ cm}^2$ for these molecules, the picosecond results show that the relative strength of the excited -singlet absorption is opposite to the apparent absorption observed on the nanosecond timescale. These results are consistent with enhanced triplet populations for the heavier-metal molecules during the longer pulses.

The nonlinear transmission functions for reverse saturable absorbers are expected to range from $T_{\text{lin}} = \exp(-\sigma_g N_0 L)$, for low incident fluences, to a saturated transmission, $T_{\text{sat}} = \exp(-\sigma_e N_0 L)$, for high degrees of excitation. When the pulse width is short compared to the excited-state (say the triplet) lifetime, we can define a saturation fluence, $F_{\text{sat}} = h\nu/\sigma_g \Phi_t$. At such high fluences, the ground-state population is largely depleted and excited-state population is distributed between the first excited -singlet and lowest-triplet states. A figure of merit for RSA molecules involving excited -singlet and triplet states can be defined as

$$\sigma_{\text{eff}}/\sigma_g = \ln T_{\text{sat}}/\ln T_{\text{lin}} \approx (\sigma_s f_s + \sigma_t f_t)/\sigma_g$$

where σ_{eff} is an effective excited-state cross section and f_s and f_t are average fractional populations of the excited -singlet and triplet states during the pulse.

From Fig. 2, we estimate that $T_{\text{sat}} \sim 0.07$ for InPc. For this molecule f_t (Table 1) is 0.95, so we can ignore f_s . Using a typical value of σ_t for MPc's of $50 \times 10^{-18} \text{ cm}^2$, we calculate $T_{\text{sat}} = 0.02$. This value is smaller than that observed, yet the fluence exiting the sample was about equal to F_{sat} (0.24 J/cm^2 for InPc), suggesting that uniform on-axis saturation was being approached. In any case, we can use the high fluence transmittance to place a lower bound on $\sigma_{\text{eff}}/\sigma_g$ for the various molecules. The cross section ratios range from 10 to 16 for the group 111A MPc's and from 10 to 18 for the group IVA MPc's as the metal becomes heavier. As a

comparison, the fullerene C_{60} has been reportedly to have a σ_t / ϵ_r about 3 at 532 nm, and a $\Phi_t \geq 0.96$.

We have investigated the performance of the heavy-atom phthalocyanines in a simple optical limiting geometry, Figure 4 shows the optical limiting response in an f/8 geometry of PbPc compared with those of the CAP and SiNc, which was previously, to our knowledge, the strongest known absorptive optical limiting dye for nanosecond 532-nm pulses. The strong signal output of the PbPc is lower by factor of 4 and 1.5 compared to CAP and SiNc, respectively. More importantly, the maximum allowable input energy for 3 microjoules output energy, i.e. the energy corresponding to 50% probability for retinal damage to eyes, is a factor of 16 and 2 higher than for CAP and SiNc, respectively. These results demonstrate the enhanced capability (i.e., nonlinear suppression of nanosecond 532 nm pulses by a factor of 81 for a limiter with a linear transmission of 30%, in a f/8 optical system) of the heavy-atom phthalocyanines for optical limiting applications. Recently, strong optical limiting has also been reported for a Pb(tetrakis-cumylphenoxy)Pc derivative.¹³ It should be emphasized that the optical limiting geometries utilized are far from optimal. Recent device modeling¹⁴ suggests that heavy-atom phthalocyanine materials in optimized optical limiter designs that ensure uniform saturation could produce attenuations of 10^4 for devices with 70% linear transmission.

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Figure Captions

Figure 1. Electronic absorption spectrum of bis(tri-(n-hexyl)siloxy)SnPc in toluene solution, at 7.1×10^{-6} mol/L. Also shown (connected dots) is the transient absorption spectrum (arb. units) of SnPc in toluene obtained 100 ns after excitation at 355 nm.

Figure 2. Nonlinear transmittance of group 111A (upper set: Al, o; Ga, Δ , In, \square) and IVA (lower set: Si, +; Ge, \square ; Sn, \bullet) metal substituted phthalocyanines in toluene solution measured using 8 ns, 532 nm laser pulses and an f/40 optical geometry. Solutions had 84% linear transmission at 532 nm for a 1-cm path length which corresponds to a concentration of 1.4×10^{-4} mol/L for IHA and IVA metal Pc's, respectively. The upper curves have been displaced vertically by 0.4, for presentation.

Figure 3. $F/8$ optical limiting response of PbPc and SiNc in toluene and CAP in methanol, at 532 nm. Input lens: 2.5 cm diameter, 4 cm focal length; laser beam diameter of 4.8 mm ($FW1/e^2M$) at the lens; calculated beam waist of 10 μm ($HW1/e^2M$); focus close to the exit window of the 1 cm cell. The transmitted energy was collected at $-f/2$ and relayed to a 1.5 mm spot size on a 1 cm diameter detector. Solutions had a linear transmittance of 0.3 at 532 nm; concentrations were 7×10^{-4} M for SiNc, 9×10^{-4} M for CAP, and 1.3×10^{-3} M for PbPc.

Table 1. Photophysical properties for group 111A and IVA metal phthalocyanines.

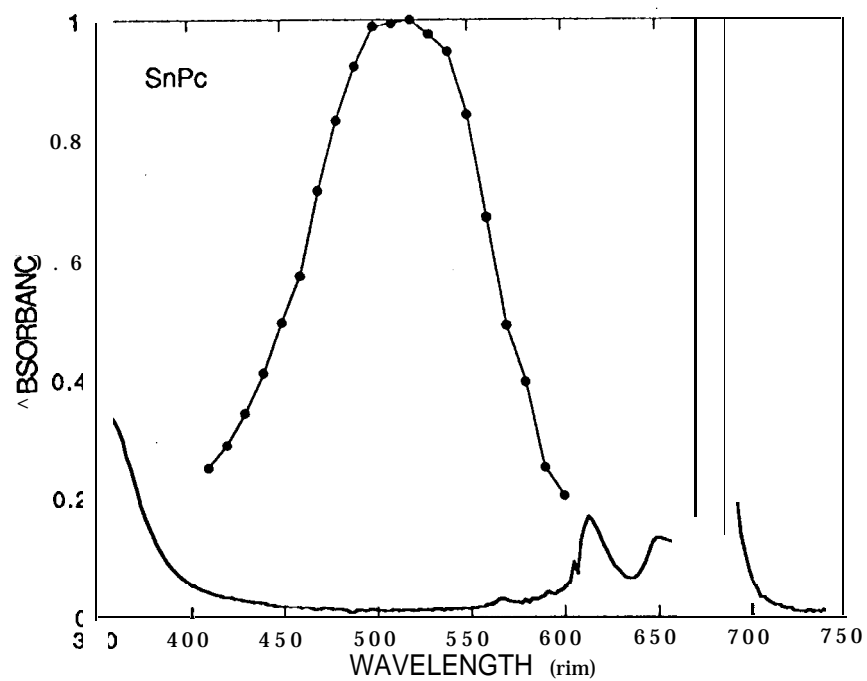
Metal	τ_s (ns) ^a	ϕ_t ^b	f_t (δ ns)
Al	6.9	0.35	0.18
Ga	3.3	0.51	0.42
In	0.3	0.88	0.95
Si	4.5 ^c	0.35 ^d	0.25
Ge	4.2 ^c	0.37 ^d	0.28
Sn	2.0 ^c	0.62	0.63
Pb	0.35	0.92	0.95

a) Determined by picosecond pump/probe measurements at 700nm, uncertainty is* 10%.

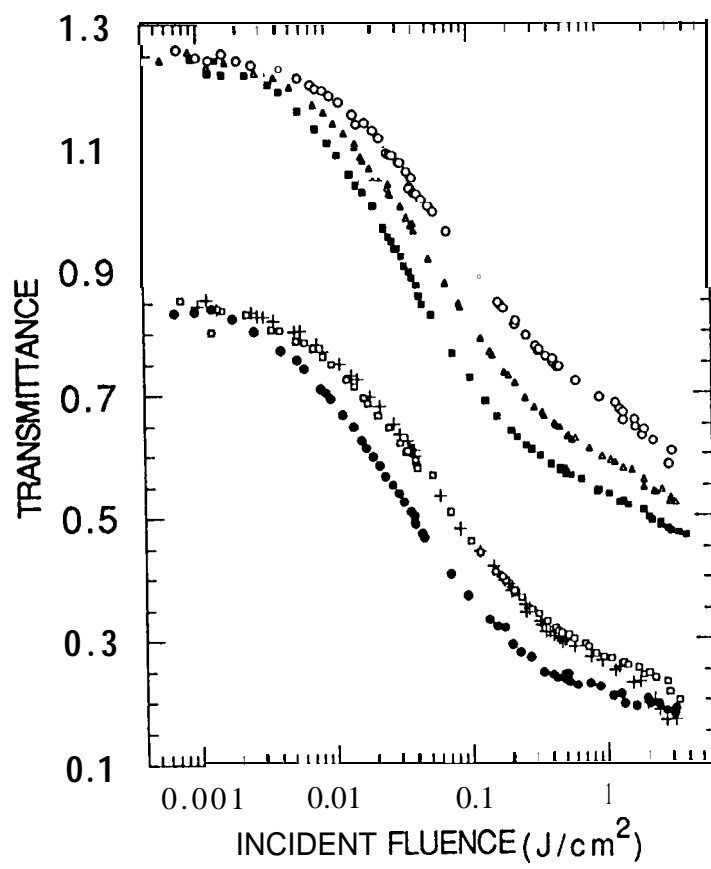
b) Determined from **ground-state bleaching** recovery at 700nm, uncertainty is ± 0.10 ,

c) Determined using **time-correlated** photon counting.

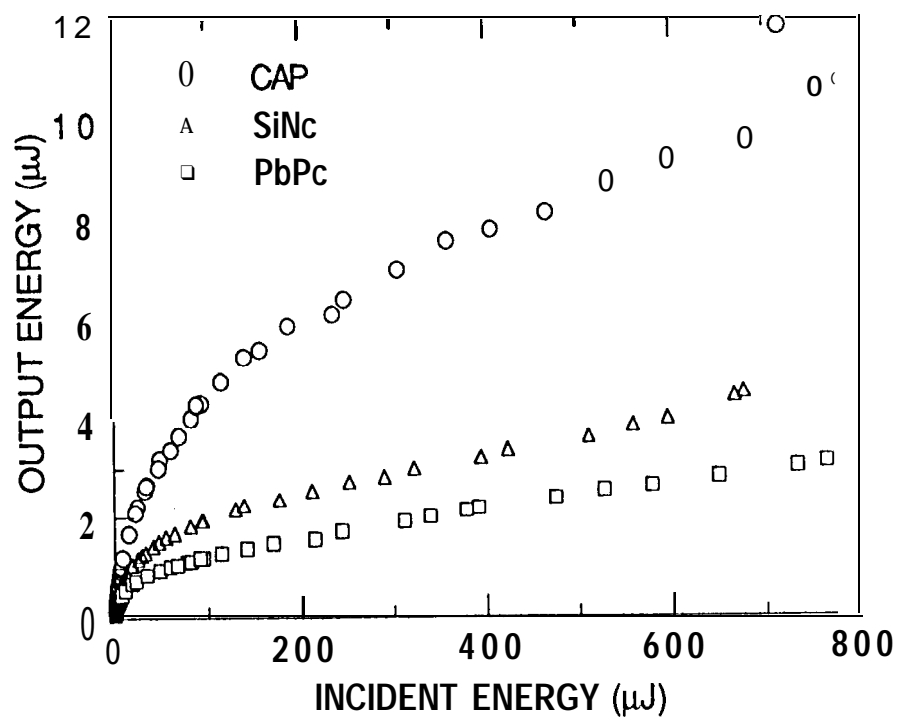
d) Estimated from fluorescence quantum yields.



Perry et al. Fig. 1



Perry et al. Fig.2



Perry et al. Fig. 3